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852,306



Date of Application and filing Complete Specification Jan. 16, 1959.

No. 1736/59.

Application made in Germany on Feb. 1, 1958.

Complete Specification Published Oct. 26, 1960.

Index at acceptance:—Class 2(5), R22(A: C6: L1A).

International Classification:—C08g.

COMPLETE SPECIFICATION

Process for the Production of Polyamides in Spheroidal Form from Cyclic Lactams

We, FARBENFABRIKEN BAYER AKTIEN-GESELLSCHAFT, a body corporate organised under the laws of Germany, of (22c), Leverkusen Bayerwerk, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with a process for the production of polyamides in the form of spheroids resembling pearls from cyclic lactams.

For the conversion of polyamides produced from cyclic lactams into formed bodies, in most cases the viscous polyamide melts obtained during the production are not worked up directly. On the contrary, these are spun from the polymerisation autoclave in the form of a strip of coarse thread and the strip or coarse thread is converted into a granulate by chopping up or cutting up. This granulate can then be washed with water and dried in order to remove any monomeric lactam which is still present. The granulate can then be stored or transported and can, according to requirements, be worked up *via* the fused masses with injection moulding machine to give formed bodies or with extruders to give threads, bristles, films, hollow bodies or hollow foils.

The present invention renders possible the production of polyamides from cyclic lactams in such a manner that they are obtained immediately in a suitable spheroidal form for storing, transporting or further working up so that a special spinning to threads and the cutting up of the threads is omitted.

The process according to the invention consists in that polymerisable cyclic lactams are suspended in inert fluids or melts in which the lactams are insoluble or only slightly soluble at temperatures lying above the melting point of the lactam but below the softening

point of the polyamide, known catalysts, and possibly accelerators and dispersion agents are added thereto, the mixture is brought to the polymerisation temperatures within the mentioned range and, at the end of the polymerisation, the polymerisate is separated off and, if necessary washed and dried in a known manner.

In this manner, the greater part of the polymerised lactam is obtained in the form of uniform and more or less well-formed spheroids which can easily be separated, for example, by decanting or filtering from the suspension agent. The so-obtained spheroidal bodies are, if desired, after washing with water and drying, suitable, without further treatment, for working up with the usual type of apparatus, such as worm presses, injection moulding machines and extruders.

As already mentioned the polymerisation of the lactam in the process according to the present invention takes place at a temperature which lies above the melting point of the lactam but below the softening point of the polyamides obtained therefrom. That the polymerisation of this type of lactam can be carried out at such temperatures, is certainly known but, hitherto, this reaction condition had only been used in the case of block polymerisation. In the case of the present process, the polymerisation is preferably commenced at temperatures which lie only slightly above the melting point of the lactam and the temperature is increased with advancing polymerisation, for example, in the course of about 1—5 hours to, for example, 100—150° C. The temperatures used initially and in the course of the polymerisation influence the size of the spheroidal bodies obtained. The higher the temperature chosen, the finer the size of the polymerisate obtained.

In order to bring the melted lactam into a fine state of division in the suspension agent, it is generally expedient to stir the mixture

well. The speed of stirring also influences the size of the spheroidal bodies: the slower the stirring the larger the size of the spheroidal bodies. On the other hand, however, the speed of stirring has only a slight influence on the yield of polyamide spheroidal bodies.

All lactams known for the production of polyamides are suitable for the present process, especially ϵ -caprolactam, the ϵ -methyl caprolactam and the lactams of ω -amino-oenanthic acid and ω -aminoundecanoic acid.

As inert fluids or melts which do not dissolve the lactam or only slightly dissolve the lactam when hot, there are preferably used long-chain, saturated, aliphatic hydrocarbons or their technical mixtures or also their mixtures with other solvents. There may be especially mentioned, for example, paraffinic oils and paraffins with solidification points between about 40° C. and 75° C. Silicone oils are also very suitable. These materials dissolve, for example, ϵ -caprolactam at temperatures up to about 100° C., sufficiently slightly in order to be suitable for the process.

The concentration of the lactams to be polymerised in suspension agents of this type can vary within wide limits. Suitable concentrations lie, for example, between about 15 and about 60% by weight.

As catalysts there may be mentioned especially alkaline compounds, such as alkali metals, alkali metal and alkaline earth metal hydrides, alkali metal carbonates and alkali metal salts of phenols or carboxylic acids.

Amongst the accelerators which may possibly be used, there may be mentioned, for example, isocyanates, carbodiimides and cyanamides, as is described, for example, in Specification No. 842,576. Nevertheless, all other suitable catalyst-accelerator combinations are also suitable for the present process.

In order to prevent the sticking together of the polyamide resulting by the polymerisation into large lumps or to prevent it adhering to the wall of the reaction vessel, it is, as already mentioned, also expedient to add a dispersion agent. Finely-divided solid compounds which are inert to the catalyst and accelerators and do not dissolve in the suspension agent act as such dispersion agents. The most suitable dispersion agents are polyamide powders of the same kind as the polyamide to be produced in spheroidal form. In this manner, the desired object is achieved without the use of foreign material which would possibly have to be again removed from the polyamide at the termination of the polymerisation. Since, in the case of the present application, a definite part of the polyamide is generally obtained in the form of a more or less fine powder, it is most expedient to add a definite amount of the polyamide powder to the new starting material at the very beginning, the polyamide powder added being

a by-product obtained from a previous polymerisation reaction.

When pigments are added to the starting mixture, for example, carbon black or titanium dioxide, the pigments are included into the polyamide spheroidal bodies obtained.

For the working up of the reaction mixture it is generally preferred to filter the mixture. After drying the polyamide spheroidal bodies separated in this manner, most of the polyamide powder obtained in small amounts at the same time can be separated off by sieving. The filtrate usually still contains a little monomeric lactam which can be used again in a subsequent polymerisation.

The following examples are given for the purpose of illustrating the invention:—

EXAMPLE 1.

100 g. ϵ -caprolactam, 200 g. of a hydrated kerosene mixture (b.p. 70—105° C./10 mm.) and 5 g. polyaminocaproic acid powder (grain size $<300 \mu$) are heated in a well-cleaned 500 cc 3-necked flask provided with a thermometer, stirrer and descending condenser. 54 g. of the hydrated kerosene mixture are distilled off under water pump vacuum in order to remove any traces of moisture still present. After the addition of 300 mg. sodium and 2 cc phenyl isocyanate, the mixture is maintained at 80° C. for one hour, then brought to 100° C. in the course of $\frac{1}{2}$ hour, to 110° C. in the course of a further $\frac{1}{2}$ hour and then maintained at this temperature for 45 minutes. The mixture is hot filtered. The residue of 62 g. moist polyamide is dried *in vacuo* at 130° C. The 54 g. of dry product obtained consists of 45 g. polyamide spheroids with a diameter of about 1 mm and 9 g. polyamide powder with a grain size of $<300 \mu$. Extendable threads can be drawn from the polyamide spheroids after melting.

EXAMPLE 2.

50 g. ϵ -caprolactam, 200 g. of a hydrated kerosene mixture, 5 g. polyaminocaproic acid powder (grain size $<300 \mu$) and 0.5 g. carbon black are polymerised in the manner described in Example 1 with the addition of 150 g. sodium and 0.5 cc. *n*-butyl isocyanate. 20 g. dry, black pigmented polyamide are obtained comprising 16 g. spheroidal bodies with a diameter of about 1 mm and 4 g. powder with a grain size of $<300 \mu$.

EXAMPLE 3.

70 g. ϵ -caprolactam, 150 g. paraffin with a solidification point of 42° C. and 5 g. polyaminocaproic acid powder (grain size $<300 \mu$) are heated in the apparatus described in Example 1. 22 g. ϵ -caprolactam are distilled off under a water pump vacuum in order to remove any traces of moisture still present. After the addition of 150 mg. sodium, the temperature is maintained at 130° C. for one

hour, is then cooled to 80° C. and 1 cc phenyl isocyanate added at this temperature. The temperature is maintained at 80° C. for two hours and then increased to 130° C. in the course of 1½ hours. The reaction mixture is hot filtered and the residue, a mixture of polyamide in spheroidal powder form, washed with cyclohexane. After washing with water and drying, there are obtained 16 g. spheroidal bodies with a diameter of approximately 2 mm and 2.5 g. powder with a grain size of <300 μ.

EXAMPLE 4.

120 g. ε-caprolactam and 1 g. talcum as dispersion agent are heated in a 500 cc 3-necked flask is provided with a thermometer, stirrer, tube for introducing nitrogen and descending condenser and 20 g. lactam are distilled off *in vacuo* (20 mm Hg) for the removal of residual amounts of moisture. After cooling in a stream of nitrogen to 80° C., 2.09 mol% potassium are added. After a short time, about 10—15 minutes, the formation of the potassium-lactam compound is completed. 200 g. silicone oil are added as suspension agent, the temperature being maintained at 80° C. Subsequently, 0.25 ml. hexamethylene diisocyanate are added as accelerator. The temperature is increased to 110° C. After about 5 minutes the reaction commences and leads to the formation of spheroidal bodies. After three hours the reaction is broken off. The yield of polyamide, preferred to the amount of lactam used, amounts to 99% of which 90% are spheroidal bodies. The relative viscosity of the spheroidal bodies in 1% by weight solution in cresol amounts to 4.52 at 25° C.

EXAMPLE 5.

The procedure described in Example 4 is repeated but without the use of a dispersion agent. Furthermore, only 1.78 mol % potassium are used, together with 0.25 ml. phenyl isocyanate and 0.25 ml. hexamethylene diisocyanate as accelerator. The polyamide yield amounts to 97% of which 60% are spheroidal bodies. The relative viscosity in 1% by weight cresol solution amounts to 3.33 at 25° C.

WHAT WE CLAIM IS:—

1. Process for the production of polyamides in spheroidal form, wherein a monomeric, polymerisable cyclic lactam is suspended in an inert fluid or melt in which said lactam is insoluble or only slightly soluble at a temperature above the melting point of the lactam but below the softening point of the polyamide, and the lactam polymerised at a temperature within the above-defined range.

2. Process according to Claim 1, wherein a polymerisation catalyst is added to the polymerisation mixture.

3. Process according to Claim 2, wherein the catalyst is an alkali metal, an alkali metal or alkaline earth metal hydride, an alkali metal carbonate or an alkali metal salt of a phenol or of a carboxylic acid.

4. Process according to Claim 1 or 2, wherein an accelerator and/or dispersion agent is added to the polymerisation mixture.

5. Process according to Claim 4, wherein the accelerator is an isocyanate, a carbodiimide or a cyanamide.

6. Process according to Claim 4, wherein the dispersion agent is a finely-divided, solid material which is inert to the catalyst and accelerator and does not dissolve in the suspension agent.

7. Process according to any of the preceding claims, wherein the lactam used is ε-caprolactam, an ε-methylcaprolactam or a lactam of ω-aminoanthoic acid or ω-amino-undecanoic acid.

8. Process according to any of the preceding claims, wherein the concentration of lactam in the suspension agent is between 15 and 60% by weight.

9. Process according to any of the preceding claims, wherein the suspension agent is a long-chain, saturated aliphatic, hydrocarbon, a technical mixture of such hydrocarbons, or a mixture of such hydrocarbons with a solvent or a silicone oil.

10. Process according to Claim 9, wherein the hydrocarbon is a paraffin oil or a paraffin with a solidification point between about 40° C. and about 75° C.

11. Process according to Claim 6, wherein the dispersion agent is a polyamide.

12. Process according to Claim 11, wherein the polyamide is the same as that which is produced by the process, the polyamide being used in the form of a powder.

13. Process for the production of polyamides in spheroidal form, substantially as hereinbefore described.

14. Process for the production of polyamides in spheroidal form, substantially as described in any of the specific examples.

15. Polyamides in spheroidal form, whenever produced by the process according to any of Claims 1—14.

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SPECIFICATION NO. 852306

The inventors of this invention in the sense of being the actual devisers thereof within the meaning of Section 16 of the Patents Act, 1949, are Herman Schnell, of Am Oberfeld 39, Krefeld-Uerdingen, Germany and Joachim Nentwig, of Am der Wildbahn 31, Krefeld-Bockum, Germany, both German citizens.

THE PATENT OFFICE,
10th November, 1960

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